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(21) International Application Number: PCT/EP00/04009 (22) International Filing Date: 4 May 2000 (04.05.00) (30) Priority Data: 899/99 11 May 1999 (11.05.99) CH (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): SETIABUDI, Frans [DE/DE]; Rappoltsteinerstrasse 17, D-79427 Eschbach (DE). (74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).	(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: PHOTSENSITIVE COMPOSITION <div style="text-align: center;"> $\text{---} \text{N} = \underset{\text{OR}}{\overset{\text{OR}}{\text{P}}} \text{---} \quad (I)$ </div> (57) Abstract A photosensitive polymerisable composition, which comprises at least one cyclic and/or oligomeric compound composed of structural units of formula (I), wherein R is identical or different radicals of formula $\text{---}(\text{A})\text{---O---C(O)---C(R}_1\text{)=CH}_2$, and R ₁ is hydrogen or methyl, A is a transition group, and n is an integer from 3 to 18, preferably 3 or 4 and, most preferably, 3, and the use of this composition as photostructurable solder stopping resist for the production of solder masks for printed circuit boards.		

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Photosensitive composition

The present invention relates to a photosensitive composition which is particularly suitable for use as photostructurable photoresist and which contains at least one selected phosphazene compound. The novel composition can be used, for example, as photostructurable solder resist in the production of solder masks for printed circuit boards.

Photosensitive compositions suitable for use as photostructurable photoresist are known per se. As a rule they contain at least (a) one film-forming crosslinkable polymeric compound, (b) one monomeric and/or oligomeric photopolymerisable compound and (c) one photoinitiator. These compositions can additionally contain numerous other components, for example a crosslinker, preferably a corresponding epoxy resin, fillers, and other additives.

When using a photosensitive composition as photostructurable photoresist, the photosensitive composition is usually applied in a thin layer to the material to be coated and is then irradiated image-wise with a suitable radiation. The film-forming crosslinkable polymers and/or the photopolymerisable monomeric and/or oligomeric compounds polymerise in this process. Owing to the photopolymerisation of the cited components, the solubility is reduced at the exposed sites of the resist coating compared to at the unexposed sites so that differentiation and structuration of the surface becomes possible. After irradiation, development is carried out. The action of a developer solution makes it possible to remove the unexposed sites of the coating. After irradiation and development, the remaining coating is preferably subjected to thermal aftertreatment or curing in the course of which any possibly present heat-curable component is cured, full curing being carried out, if required, with suitable irradiation prior to or after that aftertreatment.

It is assumed that the film-forming polymeric compound imparts to the cured coating, e.g. a solder mask, a large part of the required mechanical solidity. Hardness and durability of the cured coating, however, are held to result from, inter alia, the presence of a cured epoxy resin.

The demands made on the surface hardness of solder masks are very high. Therefore, to increase the surface hardness, hard fillers such as quartz powder or barium sulfate are incorporated into the coating or starting mixture. The printed circuit boards thus coated are,

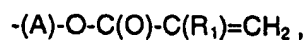
however, highly sensitive in the nickel-gold process. In particular, moisture or solvent may penetrate under the solder mask, resulting in the paint flaking off. The solder mask applied as a paint becomes more brittle if hard fillers are added. The adhesive properties are also impaired.

Surprisingly, it has now been found that the surface hardness and adhesive properties of photosensitive compositions which are suitable, for example, for use as photostructurable photoresist, in particular as photostructurable solder resist in the production of solder masks, for printed circuit boards may be substantially increased by the addition of selected polymerisable phosphazene compounds.

The present invention is defined in the patent claims. This invention relates in particular to a photosensitive polymerisable composition which is suitable for use as photostructurable photoresist, which composition comprises at least one cyclic and/or oligomeric compound composed of structural units of formula (I)



wherein R is identical or different radicals of formula



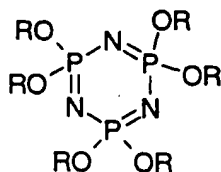
and

R₁ is hydrogen or methyl,

A is a transition group, preferably a saturated or unsaturated divalent hydrocarbon, preferably $-(C_xH_{2x})-$ or $-(C_xH_{2x-2})-$, wherein x is preferably an integer from 2 to 6, particularly preferably $-CH_2-CH_2-$, $-CH=CH-$, $-CH(CH_3)-CH_2-$, $-C(CH_3)=CH-$, more preferably $-CH_2-CH_2-$; and n is an integer from 3 to 18, preferably 3 or 4 and, most preferably, 3.

The composition preferably contains a 6-membered or 8-membered cyclic compound consisting of units of formula (I), wherein n is 3 or 4.

The composition particularly preferably contains a compound of formula (Ia):



(Ia)

wherein A, R and R₁ have the meanings given above.

The novel photosensitive composition is particularly suitable for use as photostructurable solder resist for the production of solder masks for printed circuit boards.

The invention relates in particular to a photosensitive photopolymerisable composition, which comprises at least (a) one film-forming crosslinkable polymeric compound (binder), (b) one monomeric and/or oligomeric photopolymerisable compound, (c) one photoinitiator and (d) at least one cyclic and/or oligomeric compound composed of units of the above formula (I), wherein the individual substituents have the meanings cited there, and, optionally, further additives, in particular those selected from the group consisting of the crosslinkers, preferably crosslinking epoxy resins, and fillers, dyes, pigments, defoamers, adhesion promoters, fungicides and thixotropic agents.

Functions of the compounds (a) and (b) can also be combined in a single compound or in different compounds, which lies within the scope of this invention. Thus it is possible for the monomeric or oligomeric photopolymerisable compound (b) to contain crosslinking groups, for example hydroxyl groups. The film-forming compound, for example, may also be modified such that it contains hydroxyl groups and polymerises photochemically when suitably irradiated.

Furthermore, this invention relates to solder masks which are obtainable from a composition of this invention.

In another of its aspects, this invention relates to printed circuit boards which are coated with a solder mask of this invention.

This invention also relates to the use of the novel compositions for the production of solder masks for printed circuit boards.

The compounds of formula (I) are known per se and can be prepared in a manner known per se. Compounds of formula (Ia) can be prepared, for example, by reacting 1,1,3,3,5,5-hexachlorocyclotriphosphazene with a compound of formula (II):



wherein A and R₁ have the meaning cited above.

The novel photosensitive composition contains the cyclic and/or oligomeric phosphazene compound, which is composed of units of formula (I), or a mixture of such compounds, preferably in a concentration of 0.2% to 10%, more preferably of 1.0% to 5.0% and, particularly preferably, of 1.5% to 3.7%, based on the dry weight of the components (a), (b), (c), (d) of the composition. Surprisingly, it has been found that already at a concentration of only 0.2%, preferably 1%, to 3% the surface hardness and adhesive properties can be substantially increased.

The film-forming crosslinkable polymeric compound of component (a) (also called "binder") preferably comprises epoxy acrylates. Component (b) is preferably radically polymerisable monomers such as acrylates and/or methacrylates. A possibly present hardener is, for example, a hydroxyl group-containing compound with which the component (a) can be thermally crosslinked after irradiation and development. The radically polymerisable compound (b), or part of these compounds, preferably also contains hydroxyl groups.

Compositions based on a binder, a photopolymerisable compound and a photoinitiator are described, inter alia, in EP-0 115 354. In accordance with this invention, these compositions can be used, for example, for the further processing according to this invention, i.e. in admixture with at least one cyclic and/or oligomeric phosphazene compound composed of units of formula (I) as further component.

Other photosensitive compositions are described, inter alia, in EP-0 493 317. These compositions contain water-soluble or dispersible, solid, crosslinkable film-forming polymers as binders, water-soluble or dispersible photopolymerisable acrylate monomers and/or methacrylate monomers and/or corresponding oligomers as well as water-soluble and/or dispersible photoinitiators. If the binder is not self-crosslinking, then the cited composition comprises water-soluble and/or dispersible crosslinkers for the binder polymers as thermal hardeners, selected from the group consisting of the epoxy resins, melamine resins and blocked polyisocyanates. Preferred compositions are those with carboxyl group-containing acrylate and methacrylate polymers or copolymers as binders, in which the carboxyl groups are in each case reacted with ammonia and/or specific amines so that the binder is water-soluble. Such compositions are also suitable for the further processing in admixture with at least one cyclic and/or oligomeric phosphazene compound composed of units of formula (I) as further component.

Compositions of this invention can contain as film-forming crosslinkable polymeric compound in general solid, crosslinkable, film-forming polymers. Such film-forming polymeric binders are, for example, polyvinyl alcohol/polyvinyl acetate polymers or copolymers, maleic anhydride/vinyl ether copolymers, maleic anhydride/styrene copolymers and acrylic acid and methacrylic acid polymers or copolymers as well as carboxyl group-containing acrylate and methacrylate polymers or copolymers.

The cited polymers are known per se (see e.g. in "Ullmanns Encyclopädie der technischen Chemie", 4. Ed., Vol. 19, Verlag Chemie, Weinheim 1980) and some are commercially available. Their number average molecular weight (M_n) is preferably in the range from 2'000 to 500'000, particularly preferably above 10'000. Suitable maleic anhydride/vinyl ether copolymers can contain e.g. vinyl methyl ether as ether component and are obtainable e.g. under the name Gantrex® AN (GAF CORP.). Suitable maleic anhydride/styrene copolymers are commercially available e.g. under the name Scripset® resins (MONSANTO). Polyvinyl alcohols can contain, for example, anhydrides of dicarboxylic acids, e.g. maleic anhydride, as copolymer. Copolymers of polyvinyl acetate e.g. with crotonic acid can also be used and have good film-forming properties.

Acrylic acid and methacrylic acid polymers or copolymers as well as carboxyl group-containing acrylate and methacrylate polymers or copolymers are understood to mean both the

homo- and copolymers of the pure acids and the copolymers of the acids with their esters, preferably the alkyl esters, and other comonomers such as maleic acid, itaconic acid, their esters, or styrene. Other suitable binder polymers of this type are disclosed in EP-0 115 354, some of which are commercially available.

The polymers suitable as binders must be crosslinkable, for example self-crosslinking polymers. These polymers contain structural elements which enter a crosslinking reaction solely under the influence of heat and/or actinic radiation without the addition of hardeners. Examples to be mentioned are acrylate copolymers and methacrylate copolymers which have been prepared using acrylamide monomers and/or methacrylamide monomers, for example $\text{CH}_2=\text{CH}-\text{COONH}-\text{CH}_2\text{OR}$, and which are crosslinkable through heating. A commercially available acrylic resin is, for example, the Carboset® Type 531 (GOODRICH).

Suitable self-crosslinking binder polymers are also reaction products of standard epoxy resins, for example based on (i) bisphenols, e.g. based on bisphenol A, or novolaks, with (ii) at least one aromatic di- or trihydroxy compound and (iii) triglycidyl isocyanurate in an amount of 1-30%, based on the entire composition. Such compounds are described, inter alia, in EP 0 559 607.

Suitable self-crosslinking binder polymers are also standard epoxy resins, for example based on bisphenols, e.g. based on bisphenol A, or novolaks, which have been reacted or modified to such a degree with acrylic acid and/or methacrylic acid that they are film-forming and, under suitable irradiation, polymerise photochemically and self-crosslink.

If the binder polymers used are not self-crosslinking then the novel compositions contain as further component a crosslinker (hardener), preferably selected from the group consisting of the epoxy resins, melamine resins and blocked polyisocyanates. In principle, it is of course also possible to use mixtures of the cited crosslinkers.

Suitable crosslinkers are standard epoxy resins, for example based on bisphenols, such as bisphenol A, or based on novolaks, hydantoins, uracils and isocyanurates. They may be both monomers and prereacted adducts with polyamines, polycarboxylic acids, polyalcohols or polyphenols, etc. Suitable epoxy resins are commercially available in many forms. A

particularly preferred composition comprises an epoxy resin, e.g. based on novolak, as sole thermal hardener.

Compositions of this invention can also contain a melamine resin as thermal hardener, in particular as sole thermal hardener, preferred melamine resins being condensates of melamine and formaldehyde. These may effect three-dimensional crosslinking for example by reaction with hydroxyl groups at the binder polymer. Melamine resins suitable for this invention are commercially available e.g. under the name Cymel®.

Blocked polyisocyanates suitable for this invention may be derived e.g. from aliphatic, cycloaliphatic, aromatic or araliphatic compounds containing at least two isocyanate groups, including e.g. 2,4-diisocyanatotoluene and its technical mixtures with 2,6-diisocyanatotoluene, 2,6-diisocyanatotoluene, 4,4'-diisocyanatodiphenylmethane and also technical mixtures of different diisocyanatodiphenylmethanes (for example of the 4,4'- and 2,4'-isomers), N,N'-di-(4-methyl-3-isocyanatophenyl)urea, 1,6-diisocyanatohexane and the like. They can be blocked with different radicals. Suitable blocking components are, for example, β -dicarbonyl compounds, such as malonate, acetoacetate or 2,4-pentanedione, or hydroxamate, triazoles, imidazoles, imidazolides, tetrahydropyrimidines, lactams, oximes, hydroxyimides, such as N-succinimide, or phenols or thiophenols. It is also possible to use urethanised, carbodiimidised or di- or trimerised polyisocyanates, e.g. urethanised 4,4'-diisocyanatodiphenylmethane, carbodiimidised 4,4'-diisocyanatodiphenylmethane, the uretdione of 2,4-diisocyanatotoluene or the trimer of diisocyanatotoluene. The deblocking temperature of the blocked polyisocyanates is preferably from 90°C to 160°C, more preferably from 110°C to 140°C. Polyisocyanates suitable according to this invention are also commercially available, e.g. under the name Desmodur® (BAYER). Novel compositions containing a blocked polyisocyanate, in particular as sole thermal hardener, are also a preferred embodiment of this invention.

Particularly preferred compositions of this invention are those which contain as component (a) acrylic acid and/or methacrylic acid polymers and/or acrylic acid and/or methacrylic acid copolymers and/or carboxyl group-containing acrylate and/or methacrylate polymers and/or acrylate and/or methacrylate copolymers which are soluble or insoluble in water and/or which are copolymerised with glycidyl acrylate and/or glycidyl methacrylates.

Suitable photopolymerisable acrylate or methacrylate monomers and oligomers are known to the skilled person and are mentioned e.g. in the above-cited EP-A-0 115 354 which is referred to here. Suitable for use in this invention are, for example, diethylene glycol diacrylate, trimethylolpropanetriacrylate, pentaerythritoltriacrylate or epoxy acrylates, e.g. those derived from bisphenol A, phenol novolaks or cresol novolaks which may contain both epoxy groups and acrylate and/or methacrylate groups, urethane acrylates or polyester acrylates. The epoxy acrylates can usually also be modified with a carboxylic anhydride.

The photoinitiators used may be customary initiators of radical photopolymerisation, if required together with coinitiators. The initiators are preferably present in an amount of 0.1 to 10% by weight of the composition and could per se also be present in amounts of more than 10 % by weight, but this usually does not give any better results. Suitable examples of photoinitiators or photoinitiator systems are aromatic carbonyl compounds, such as benzoin, benzoinalkyl ether, e.g. isopropyl ether or n-butyl ether, α -substituted acetophenones, in particular benzilketals, such as benzildimethylketal, or α -halogen-substituted acetophenones, such as trichloromethyl-p-tert-butylphenylketone or morpholinomethylphenylketone, or dialkoxyacetophenones, such as diethoxyacetophenone, or α -hydroxyacetophenones, such as 1-hydroxycyclohexylphenylketone; or benzophenones, such as benzophenone or bis(4-dimethylamino)benzophenone; or metallocene initiators, e.g. titanocene initiators, such as bis(π -methylcyclopentadienyl)-bis(σ -pentafluorophenyl)-titanium-IV; or a stannane in combination with a photoreducible dye, for example trimethylbenzylstannane in combination with methylene blue or bengal pink; or a quinone or a thioxanthone in combination with an amine which contains at an α -C-atom at least one hydrogen atom, such as anthraquinone, benzoquinone or thioxanthone in combination with bis(4-dimethylamino)-benzophenone or triethanolamine; or a thioxanthone, for example an alkyl- or halogen-substituted thioxanthone, e.g. 2-isopropylthioxanthone or 2-chlorothioxanthone; or acylphosphides.

The novel compositions can comprise fillers, the novel addition of the compound or compounds of formula (I) being able to reduce the amount of filler. Suitable fillers are, for example, talcum, barium sulfate or quartz, with which e.g. the properties of a coating, such as its surface hardness, heat resistance or isolation capacity against electric currents, may be improved or with which the tackiness may be reduced. The novel compositions can contain

fillers in amounts from 10 % by weight to 50, preferably to 35 % by weight, based on the entire weight of the composition.

The novel compositions can contain additional additives. Such additives are, for example, dyes and/or pigments, preferably in an amount from 0.1 to 1 % by weight, or customary additives, such as defoamers, adhesion promoters, fungicides or thixotropic agents, preferably each in amounts from 0.5 % by weight to 5 % by weight, based on the entire weight of the composition.

To prepare the novel compositions, the per se known components (a), (b) and (c) and any other components and additives which may be present are mixed in a manner known per se, if required with heating and melting, and a compound of formula (I) or a mixture of such compounds is added before, during or after the mixing of the individual components of the mixture. The skilled person is familiar with how to do this.

The novel photosensitive composition is suitable in particular for the preparation of coatings. This invention therefore also relates to a process for the preparation of a coating, in particular of solder masks, which comprises applying a novel composition to a substrate, removing any solvent possibly present, irradiating the coating obtained with actinic radiation in a desired pattern, removing the unexposed sites of the coating by means of a suitable solvent with exposure of the substrate, and then thermally curing the coating remaining on the substrate and, if required, curing it before or after the thermal curing by means of UV radiation.

After coating, the solvent which may be present in the composition (e.g. organic solvent or water) is usually removed by drying. An amorphous resist film is obtained on the substrate, the thickness of which after drying is preferably from 5 μ m to 150 μ m. The temperatures during drying are normally below the temperature at which the thermal crosslinking of the binder in the coating takes place, preferably below 100°C, more preferably at about 70°C - 80°C. Drying can also be carried out under vacuum, optionally without heating.

The photosensitive coating is then exposed to radiation in a manner known per se in particular in order to polymerise the photochemically polymerisable monomeric and/or oligomeric compounds, for example the acrylate and/or methacrylate monomers and/or the corresponding oligomers. This is usually carried out image-wise. Owing to the photopolymerisation of

the cited components, the solubility is reduced at the exposed sites compared to at the unexposed sites so that a differentiation of the surface due to a different solubility in suitable solvents is obtained.

The irradiation of the novel compositions is preferably carried out with actinic radiation. This is usually UV- and/or VIS-radiation, preferably of the wavelength from about 220nm to 550 nm, in particular from 220nm to 450 nm. Any of the radiation sources known per se may be used for irradiation, for example mercury high pressure lamps or UV-/VIS-laser. The process parameters, such as irradiation time and distance from the source of radiation and from the photosensitive coating, generally depend on the kind of photosensitive composition used and on the desired properties of the coating, and the skilled person can determine them with a few routine tests. The image-wise irradiation can be carried out, for example, through a photomask or through the direct writing of a laser beam on the photosensitive coating.

Development is carried out after the irradiation. Through the action of a developer solution the unexposed sites of the photoresist can be removed in a manner known per se with suitable aqueous or organic solvents.

After irradiation and development, the coating is subjected to a thermal aftertreatment or cure. This is done by heating to a temperature at which preferably a total crosslinking of the binder polymer and of the compound of formula (I) takes place. The temperature required therefor is usually above 100°C, e.g. in the range from 120°C - 180°C, preferably from 120°C - 150°C. It may be of advantage to also carry out a further cure with UV radiation which may result in a more complete polymerisation in particular of the component (b) and of the compound of formula (I). This can take place, for example, at the same time as the thermal curing.

The preparation of the coated substrates can be carried out using coating processes known per se by means of which a coating may be uniformly applied. Examples of such coating processes are spin-coating, brush application, spray application, e.g. electrostatic spraying, reverse roll coating, immersion coating and knife coating and the curtain coating process. The curtain coating and screen printing processes are preferred.

The amount applied (coating thickness) and the kind of substrate (coating substrate) depend on the desired field of application. The novel compositions can be applied in relatively thin layers and provide good resolution. The use of the corresponding radiation source and photosensitive component makes them, in particular, suitable for all customary fields of application where the generation of structured images is desired.

The novel compositions are particularly suitable for the preparation of coatings on any kind of substrate, for example wood, textiles, paper, ceramics, glass, plastics, such as polyester, polyolefins, cellulose acetate or epoxy resins, in particular glass fibre reinforced epoxy resins, and metals, such as aluminium, copper, nickel, iron, zinc, magnesium or cobalt, and semi-conductor materials, such as silicium, GaAs or germanium, and isolator materials, such as Si_3N_4 or SiO_2 , where an image or, in particular, a protective layer, is to be applied through irradiation.

Coatings of this invention also have excellent thermal resistance if they are brought into contact with hot liquid metals and/or alloys, for example in a solder bath which usually has a temperature in the range of about 270°C . As mentioned at the outset, this use of coatings prepared according to this invention is also an object of this invention, as is also the use of the described compositions as photostructurable solder stopping resist in the production of printed circuit boards, which is very particularly preferred.

The following Examples illustrate this invention in more detail.

Example 1

The following applies in Table 1:

Example A: comparison example, without phosphazene compound

Examples B and C: according to this invention with phosphazene compound

a) Preparation of the resin paste: the crude materials (1), (2), (3), (5), (7), (8) and (9) (figures of the crude materials each according to the Tables 1 and 2) are dissolved in (6) at a temperature of $40\text{-}50^\circ\text{C}$, upon which the photoinitiator (4) and the hardener (11) are added and homogenised with dissolver. The filler (10) is then added. After cooling to room temperature the homogeneous mixture is ground in a triple roll mill.

b) Preparation of the accelerator: chlorotolurone (13) and the dye (14) according to the Tables 1 and 2 are dissolved, with stirring, in methoxypropanol (12) at a temperature of 30-40°C and are then allowed to cool to room temperature.

Application of the paint mixture

The resin paste prepared according to the above instructions of a) and b) and the accelerator mixture are mixed in the indicated ratios. At room temperature, 100 g each of resin paste are mixed with the corresponding amount of accelerator mixture so that the paint mixtures listed in Table 1 are obtained, i.e. to yield the compositions according to the mixtures A (comparison mixture) and B and C (mixtures of this invention).

Table 1

Components	A (parts by weight, e.g. g)	B (parts by weight, e.g. g)	C (parts by weight, e.g. g)
(1) binder	24.73	24.25	23.78
(2) photopolymerisable compound	25.72	25.22	24.73
(3) photopolymerisable compound	3.26	3.20	3.13
(4) photoinitiator	4.51	4.42	4.34
(5) phosphazene compound	..	1.96	3.85
(6) solvent	14.78	14.49	14.21
(7) flow control agent	0.72	0.70	0.69
(8) defoamer	0.16	0.16	0.15
(9) stabiliser	0.01	0.01	0.01
(10) filler	16.09	15.78	15.47
(11) hardener	0.59	0.57	0.56
(12) methoxypropanol	9.20	9.02	8.85
(13) accelerator	0.08	0.08	0.07
(14) dye	0.16	0.15	0.15
total	100	100	100

Table 2 (the individual components)

Components
(1) binder: reaction product of 467 g of diglycidyl ether of bisphenol A (epoxy value:5.26-5.38 val/kg), 333g of tetrabromobisphenol A. 200 g of triglycidyl isocyanurate and 0.05 g of 2-phenylimidazole, heated to 160°C over c. 3 hours. After cooling to c. 150°C, charged with 125g of methyl ethyl ketone. Prepared according to EP 0 559 607, Example 1.
(2) photopolymerisable compound: tris(2-hydroxyethyl)isocyanurate triacrylate
(3) photopolymerisable compound: ethoxylated trimethylolpropane triacrylate
(4) photoinitiator: Irgacure 819, of Ciba SC, based on phosphin oxide
(5) phosphazene compound: 1,1,3,3,5,5-hexa(methacryloyloxyethoxy)cyclotriphosphazene
(6) solvent: propylene glycol methyl ether acetate
(7) flow control agent: FC 431, of 3M, USA
(8) defoamer Byk 077, of Byk Chemie
(9) stabiliser: hydroquinone
(10) filler: talcum
(11) hardener: dicyandiamide
(12) methoxypropanol (solvent)
(13) accelerator: chlorotolurone
(14) dye: Orasol blue NG

A copper-coated laminate is coated with the paint mixture in a K Control Coater apparatus type model 625 : K303 (adjustment of the coating apparatus: K 202 knife mount bar No.9 = 125µm, absorption rate 5m/min).

The copper laminate newly coated with the paint mixture is left standing for 20 minutes in the air and is then dried for 30 minutes at 80°C. The copper laminate is exposed with UV light energy of 1500 mJ/cm², developed in a developing process with gamma-butyrolactone and then fully cured at 150°C in a circulating air oven for one hour.

Examination of the paint film (formulations A, B and C):

The tests show that the addition of the phosphazene compound (5) substantially increases the surface hardness. The phosphazene compound (5) at the same time acts as adhesion promoter on copper and also as flow control agent, i.e. in the tests B and C it is possible to forego the use of the flow control agent or to reduce its amount. However, for the sake of the comparability of the batches (with and without phosphazene compound), the flow control agent is used in all three formulations. The formulation A (without phosphazene compound) has a very bad flow and very bad adhesion on the substrate compared to the formulations B and C.

The surface hardness of the formulation A is 4-5 H (pencil hardness) and exhibits a very bad cross-hatch adhesion image (cross-hatch adhesion = 5, according to DIN 53 151). The addition of the phosphazene compound according to the formulations B and C increases the surface hardness by 2 grades to 7H. Surprisingly, these two formulations have a very good cross-hatch adhesion image of 0 (zero) according to DIN 53 151. The addition of the phosphazene compound not only increases the surface hardness (pencil hardness) by two grades but additionally increases both the adhesion of the coating on the substrate and the toughness of the coating. This is remarkable, for as a rule the harder the surface the worse the cross-hatch image.

Pencil hardness (description of the test method)

Principle: Measurement of the pencil hardness of a solder stop paint on laminate or Cu/laminate.

apparatus: TAIYU No.: 2195 (Probimer system apparatus 5246)

pencils: MITSUBISHI of 2H-9H hardness, sandpaper

test samples: laminate or Cu/laminate, size: 4cm x 15cm.

Preparation of the pencils: the pencils have a 5-6 mm long undamaged, exposed lead cylinder. The tip of the lead cylinder is held at a 90° angle to the sandpaper and abraded so that a flat round cross-section is obtained. The cross-section must be free from any irregularity, in particular at the edge.

Procedure: The test sample is fixed to the measuring device. The pencil of the highest hardness is clamped at a 45° angle and placed on the test sample. The test sample is moved by

means of the mechanical device designated therefor (crank) at least 6.5 mm towards the tip of the pencil. This procedure is repeated with the pencils of lower hardness. The test may not be carried out more than once at the same site of the test sample.

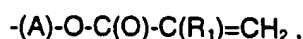
Evaluation: The pencil hardness is that hardness value at which the surface is not yet hollowed out or dented. This value is not to be confused with the scratch hardness which is that hardness value at which the surface is not yet scratched.

What is claimed is

1. A photosensitive polymerisable composition, which comprises at least one cyclic and/or oligomeric compound composed of structural units of formula (I)



wherein R is identical or different radicals of formula



and

R₁ is hydrogen or methyl,

A is a transition group, and

n is an integer from 3 to 18, preferably 3 or 4 and, most preferably, 3.

2. A composition according to claim 1, which comprises at least one cyclic 6-membered or 8-membered compound consisting of units of formula (I).

3. A composition according to claim 2, which comprises at least one phosphazene compound of formula (Ia):



wherein A, R and R₁ are as defined in claim 1.

4. A composition according to any one of claims 1 to 3, which comprises at least (a) one film-forming crosslinkable polymeric compound (binder), (b) one monomeric and/or oligomeric photopolymerisable compound, (c) one photoinitiator and (d) at least one cyclic and/or oligomeric compound which is composed of units of the above formula (I), wherein the indi-

vidual symbols each have the meanings cited in claims 1 to 3, and, optionally, further additives.

5. A composition according to any one of claims 1 to 4, wherein the functions of the compounds (a) and (b) are combined in an individual compound or in different compounds.
6. A composition according to any one of claims 1 to 5, wherein the monomeric and/or oligomeric photopolymerisable compound (b) comprises crosslinking groups.
7. A composition according to any one of claims 1 to 6, wherein the film-forming compound (a) is modified such that it polymerises photochemically when suitably irradiated.
8. A composition according to any one of claims 1 to 7, which comprises the cyclic and/or oligomeric phosphazene compound, which is composed of units of formula (I), or a mixture of such compounds, in a concentration of 0.2% to 10%, preferably of 1.0% to 5.0% and, more preferably, of 1.5% to 3.7%, based on the dry weight of the components (a), (b), (c), (d) of the composition.
9. A composition according to any one of claims 1 to 8, wherein the component (a) is an epoxy acrylate and the component (b) is a radically polymerisable monomer, preferably an acrylate and/or methacrylate, which may contain hydroxyl groups.
10. Use of the composition according to any one of claims 1 to 10 as photostructurable solder stopping resist for the preparation of solder masks for printed circuit boards.
11. A solder mask which is obtainable from a composition according to any one of claims 1 to 9.
12. A circuit board which is coated with a solder mask according to claim 11.
13. A process for the preparation of solder masks, which comprises applying a composition according to any one of claims 1 to 9 to a substrate, removing any solvent possibly present, irradiating the coating obtained with actinic radiation in a desired pattern, removing the unexposed sites of the coating by means of a suitable solvent with exposure of the sub-

strate, and then thermally curing the coating remaining on the substrate and, if required, curing it before or after the thermal curing by means of UV radiation.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/04009

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 G03F7/027		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 G03F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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X Y X	EP 0 453 237 A (FUJITSU LIMITED) 23 October 1991 (1991-10-23) page 6, line 40 - line 54 page 7, line 1 - line 22 page 14; example 8 claims 1,6,7,15,16 --- EP 0 464 749 A (CANON KABUSHIKI KAISHA) 8 January 1992 (1992-01-08) page 4, line 44 - line 58 page 5, line 1 - line 47 page 5, line 51 - line 57 --- <div style="text-align: center;">-/-</div>	1-6,8, 10-13 7,9 1-6,8
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>*"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>*"E" earlier document but published on or after the international filing date</p> <p>*"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>*"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search	Date of mailing of the international search report	
30 August 2000	12/09/2000	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Dupart, J.-M.

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